Statistical Physics: Example Sheet 1

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1. Establish Stirling's formula. Start with

$$N! = \int_0^\infty e^{-x} x^N dx \equiv \int_0^\infty e^{-F(x)}\, dx.$$

Let the minimum of F be at x_0. Approximate $F(x)$ by $F(x_0) + F''(x_0)(x - x_0)^2/2$ and, using one further approximation, show that

$$N! \approx \sqrt{2\pi N} N^N e^{-N}$$

We will mostly be interested in $N \sim 10^{23}$. But what is the accuracy of Stirling's formula for the paltry value of $N = 5$?

2i. Show that two coupled systems in the microcanonical ensemble maximize their entropy at equal temperature only if the heat capacity is positive.

ii. In the canonical ensemble, show that the fluctuations in energy $\Delta E^2 = \langle E^2 \rangle - \langle E \rangle^2$ are proportional to the heat capacity.

iii. Show that in the canonical ensemble the Gibbs entropy can be written as

$$S = k_B \frac{\partial}{\partial T}(T \log Z)$$

3. Consider a system consisting of N spin-$\frac{1}{2}$ particles, each of which can be in one of two quantum states, 'up' and 'down'. In a magnetic field B, the energy of a spin in the up/down state is $\pm\mu B/2$ where μ is the magnetic moment. Show that the partition function is

$$Z = 2^N \cosh^N\left(\frac{\beta\mu B}{2}\right)$$

Find the average energy E and entropy S. Check that your results for both quantities make sense in at $T = 0$ and $T \to \infty$.

Compute the *magnetisation* of the system, defined by $M = N_\uparrow - N_\downarrow$ where $N_{\uparrow/\downarrow}$ are the number of up/down spins. The magnetic susceptibility is defined as $\chi \equiv \partial M/\partial B$. Derive *Curie's Law* which states that at high temperatures $\chi \sim 1/T$.

4. Consider a system of N interacting spins. At low temperatures, the interactions ensure that all spins are either aligned or anti-aligned with the z axis, even in the absence of an external field. At high temperatures, the interactions become less important and spins can point in either $\pm\hat{z}$ direction. If the heat capacity takes the form,

$$C_V \;=\; C_{\rm max}\left(\frac{2T}{T_0}\;-\;1\right)\;\;\text{for}\;\;\frac{T_0}{2}\;<\;T\;<\;T_0\;\;\text{and}\;\;C_V\;=\;0\;\;\text{otherwise}\,.$$

determine $C_{\rm max}$.

5. Compute the partition function of a quantum harmonic oscillator with frequency ω and energy levels

$$E_n = \hbar\omega\left(n+\frac{1}{2}\right) \qquad n \in \mathbf{Z}$$

Find the average energy E and entropy S as a function of temperature T.

Einstein constructed a simple model of a solid as N atoms, each of which vibrates with the same frequency ω. Treating these vibrations as a harmonic oscillator, show that at high temperatures, $k_BT \gg \hbar\omega$, the Einstein model correctly predicts the *Dulong-Petit* law for the heat capacity of a solid,

$$C_V = 3Nk_B$$

At low temperatures, the heat capacity of many solids is experimentally observed to tend to zero as $C_V \sim T^3$. Was Einstein right about this?

6i. A quantum violin string can vibrate at frequencies ω, 2ω, 3ω and so on. Each vibration mode can be treated as an independent harmonic oscillator. Ignore the zero point energy, so that the mode with frequency $p\omega$ has energy $E = n\hbar p\omega$, $n \in \mathbf{Z}$. Write an expression for the average energy of the string at temperature T. Show that at large temperatures the free energy is given by,

$$F = -\frac{\pi^2}{6}\frac{k_B^2T^2}{\hbar\omega}$$

(Hint: You may need the value $\zeta(2) = \pi^2/6$)

ii*. Show that the partition function of the quantum violin string can be written as

$$Z = \sum_N p(N)e^{-\beta E_N}$$

where $E_N = N\hbar\omega$ and $p(N)$ counts the number of partitions of N. It can be shown that this formula also applies to a relativistic string if we use $E_N = \sqrt{N}\hbar\omega$. Show that the relativistic string has a maximum temperature, known as the Hagedorn temperature, $k_B T_{\rm max} = \sqrt{6}\hbar\omega/2\pi$.

(Hint: Google the Hardy-Ramanujan formula).

7. The purpose of this question is to provide a universal way of looking at all the ensembles, starting from the Gibbs entropy for a probability distribution $p(n)$,

$$S = -k_B \sum_n p(n)\log p(n)$$

i. By implementing the constraint $\sum_n p(n) = 1$ through the use of a Lagrange multiplier show that, when restricted to states of fixed energy E, the entropy is maximised by the microcanonical ensemble in which all such states are equally likely. Further show that in this case the Gibbs entropy coincides with the Boltzmann entropy.

ii. Show that at fixed *average* energy $\langle E\rangle = \sum_n p(n)E_n$, the entropy is maximised by the canonical ensemble. Moreover, show that the Lagrange multiplier imposing the constraint is proportional to β, the inverse temperature. Confirm that maximizing the entropy is equivalent to minimizing the free energy

iii. Show that at fixed average energy $\langle E\rangle$ and average particle number $\langle N\rangle$, the entropy is maximised by the grand canonical ensemble. What is the interpretation of the Lagrange multiplier in this case?

8. Let Z_N be the canonical partition function for N particles. Show that the grand partition function $\mathcal{Z}$ can be written as

$$\mathcal{Z}(\mu, V, T) = \sum_{N=0}^{\infty} \xi^N Z_N(V,T)$$

where $\xi = e^{\mu\beta}$ is called the *fugacity*. (It will be denoted z in the lecture notes but I wanted to save you from having to write three different types of z). Show that

$$\langle N\rangle = \xi\frac{\partial}{\partial\xi}\log\mathcal{Z} \quad , \quad (\Delta N)^2 = \left(\xi\frac{\partial}{\partial\xi}\right)^2 \log\mathcal{Z} \quad .$$

If $Z_N = Z_1^N/N!$ show that $\mathcal{Z}(\xi, V, T) = e^{\xi Z_1(V,T)}$. For this case, show also that

$$\frac{\Delta N}{\langle N\rangle} = \frac{1}{\langle N\rangle^{1/2}} \quad .$$

9. Make use of the fact that the free energy $F(T,V,N)$ of a thermodynamic system must be extensive, to explain why

$$F = V\left.\frac{\partial F}{\partial V}\right|_{T,N} + N\left.\frac{\partial F}{\partial N}\right|_{T,V} \quad .$$

The *Gibbs free energy* is defined as $G = F + pV$. Use the result above for F to show that the Gibbs free energy can be expressed as $G = \mu N$. Explain why this result was to be expected from the scaling behaviour of G.

10. A neutral gas consists of N_e electrons e^-, N_p protons p^+ and N_H Hydrogen atoms H. An electron and proton can combine to form Hydrogen,

$$e^- + p^+ \leftrightarrow H$$

At fixed temperature and volume, the free energy of the system is $F(T, V; N_e, N_p, N_H)$. We can define a chemical potential for each of the three species as

$$\mu_i = \frac{\partial F}{\partial N_i}$$

By minimizing the free energy, together with suitable constraints on the particle numbers, show that the condition for equilibrium is

$$\mu_e + \mu_p = \mu_H$$

Such reactions usually take place at constant pressure, rather than constant volume. What quantity should you consider instead of F in this case?